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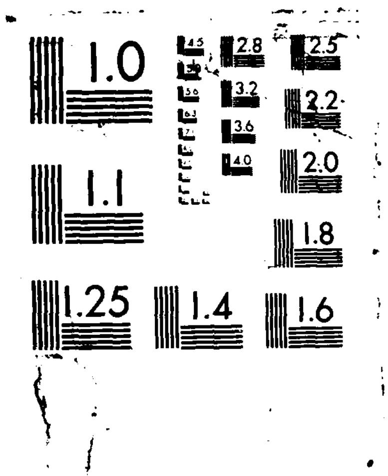
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The events that led to the discovery of high temperature superconducting materials is reviewed in a chronological fashion beginning with the discovery of superconductivity in mercury by H. K. Onnes. The signature properties of superconductivity are described, the basic theoretical framework necessary to understand superconductivity is briefly sketched, and the properties that lead to technological applications are discussed. Finally, the properties of LaBCO and YBCO are described, and the possibility of technological applications is discussed.

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The Advent of High Temperature Superconducting Materials: Chronology of Events and Hallmark Developments

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THE ADVENT OF HIGH TEMPERATURE SUPERCONDUCTING MATERIALS: CHRONOLOGY OF EVENTS AND HALLMARK DEVELOPMENTS

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1 DISCOVERY OF SUPERCONDUCTIVITY

It has been known from the earliest experiments on the electrical properties of conductors that the electrical resistivity of a metal decreases when it is cooled. At 20 to 30 K the resistance usually becomes constant at a value determined by the purity of the metal and the crystalline perfection of the specimen being measured. When metals are cooled to even lower temperatures some of them exhibit an abrupt drop in resistivity and enter a state in which there is no resistance to the flow of current. This new state was first discovered in mercury by H. Kammerlingh Onnes at the University of Leiden in the spring of of 1911 (1). Kammerlingh Onnes noted that upon cooling below 4.2 K, "Mercury has passed into a new state, which on account of its extraordinary properties, may be called a superconductive state".

The temperature at which the transition to the superconducting state occurs is designated T_c. More than 25 metallic

elements superconduct at ambient pressure, and several more do when placed under high pressure. Transition temperatures for some representative superconducting elements are given in Table 1 (2). There are several thousand superconducting alloys (3), and the highest transition temperature achieved before 1986 was 23.2 K for Nb_3Ge (4). In late 1986 and early 1987 there were tremendous advances made in the discovery and characterization of new high temperature superconducting materials, and there are now reports of superconducting transitions above room temperature.

The chronology of events and hallmark developments that led to the advances in high temperature superconductivity are briefly sketched in this tutorial paper. By necessity, certain terms are briefly defined and fundamental concepts are tightly skectched as they are encountered in the chronology. More detailed treatments of the physics of superconductors and the structural and electronic properties of high temperature superconducting materials are presented in the following papers by J. H. Miller and M.-H. Whangbo.

2 THE SIGNATURE OF THE SUPERCONDUCTING STATE

Loss of Resistivity An abrupt drop in resistivity of a metal at a characteristic temperature T_c and an apparent absence of resistance to the flow of electricity below T_c, as shown in Figure 1a, are dramatic indications that the superconducting state may be present. This was the discovery made by Kammerlingh

Table 1. Superconducting Transition Temperatures for Some Representative Elements.

Element	T_C, K	Element	T_C, K
Aluminum	1.75	Cadmium	0.517
Indium	3.408	Iridium	0.113
Lead	7.196	Mercury-α	4.154
Molybdenum	0.915	Niobium	9.25
Osmium	0.66	Protactinium	1.4
Rhenium	1.697	Ruthenium	0.49
Tantalum	4.47	Technetium	7.8
Thallium	2.38	Thorium	1.38
Tin	3.722	Titanium	0.40
Tungsten	0.0154	Vanadium	5.40
Zinc	0.85	Zirconium	0.61

Onnes in 1911. There are problems with the experimental work. Below T_c, $R = 0$, and from Ohm's law, $V = IR$, then V is also equal to zero. Very low, but finite, resistivities are difficult to determine in the laboratory, where, typically, the voltage is measured in a circuit at a constant applied current, and the resistance and resistivity are calculated. Since thermoelectric effects affect the measurement of vanishingly small voltages, it is easy to see why the measurement of very small resistivities is subject to many sources of experimental error.

The complete disappearance of resistivity may be demonstrated by making use of the properties of rings. Consider that a ring, as shown in Figure 2, is exposed to an external magnetic field of flux density $\underline{B}$, which is changing as a function of

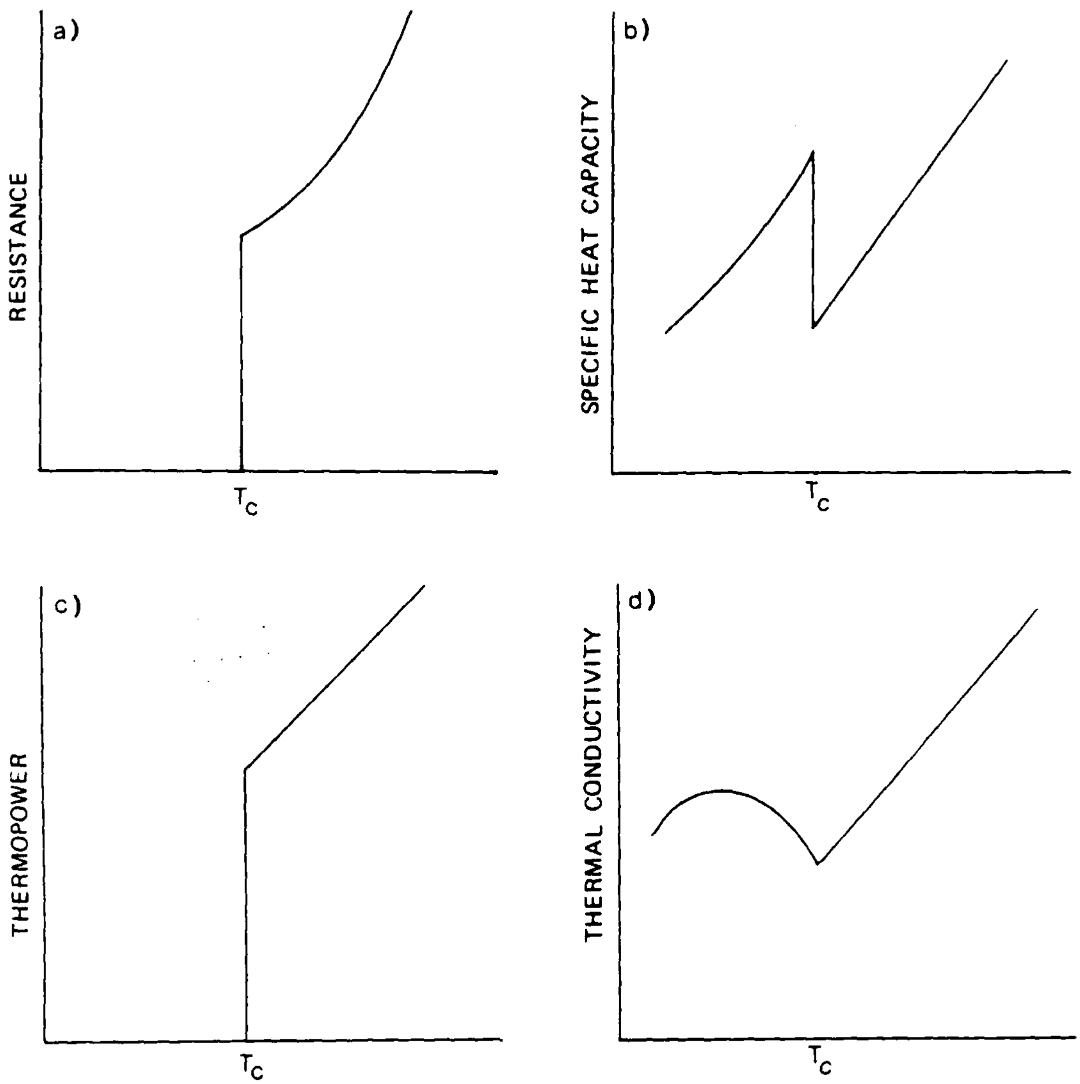

Figure 1. Temperature dependencies of the (a) resistance, (b) specific heat, (c) thermopower, and (d) thermal conductivity of a substance which undergoes a transition to a superconducting state at T_C.

time. The current $I(t)$ flowing in the ring at time t is given by Lenz's law, which states that

$$-A(dB/dt) = RI(t) + L[dI(t)/dt] \qquad (1)$$

where A is the area of the ring, R is the resistance, and L is the inducatance of the ring. If there is no external applied magnetic field, then (1) becomes the differential equation

$$RI(t) + L[dI(t)/dt] = 0 \qquad (2)$$

which has the solution

$$I(t) = I(0)\exp(-Rt/L) \qquad (3)$$

Thus, the current in the ring exponentially decays in the absence of an external changing magnetic field, and it eventually vanishes.

However, if the ring in Figure 2 becomes superconducting, then $R = 0$ and $I(t) = I(0)$. In other words, the current does not decay with time! This current is called the persistent current, and the circulation of the current gives rise to a magnetic field. Persistent currents remain without change, within the limits of detection by the most sensitive modern instruments, for many years. This property of superconducting materials is very important for high-field magnets such as those used in NMR spectrometers.

Abrupt Change in Specific Heat The abrupt increase in specific heat at T_c that occurs for superconductors is shown in Figure 1b where it may be seen that the temperature dependence of the specific heat in the superconducting state is very much different from that in the normal state. The electronic specific heat

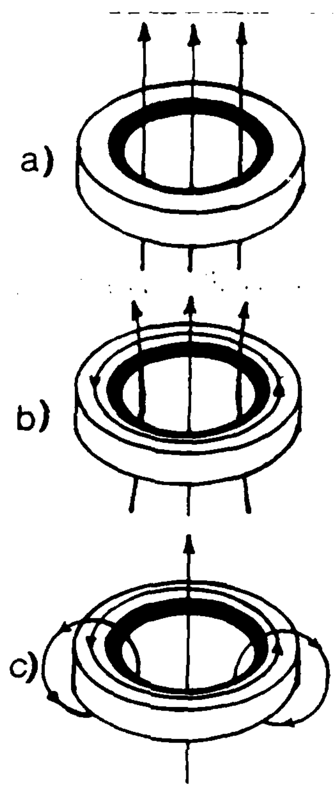

Figure 2. Schematic representation of a superconducting ring in (a) the normal state in a magnetic field showing some flux lines, (b) in the superconducting state with a current shown in the ring, and (c) in the supercconducting state with the persistent current indicated.

above T_c is given by

$$C_{en} = \gamma T \tag{4}$$

and that well below T_c is described well by

$$C_{es} = \gamma T_c a \exp(-bT_c/T) \tag{5}$$

where a and b are experimental constants of about 10 and 1.5, respectively. The exponential dependence of the specific heat in

the superconducting state suggests an average excitation energy of $1.5kT_c$, or in other words, the specific heat results suggest the existence of a gap in the electronic structure. The success of the theory by Bardeen, Cooper, and Schrieffer (BCS theory) (5) in describing this gap and the other fundamental properties of superconductors will be discussed in the next paper in these proceedings.

The existence of a gap has been confirmed spectroscopically (6), and found to be about twice that of the thermal gap (6b,c). This may be understood if the electrons occur as pairs with the spectroscopic result giving the average energy required to create a pair of excitations while the thermal result gives the energy per statistically independent particle.

<u>Thermopower and Thermal Conductivity</u> If a metal in the normal state is subjected to a temperature gradient $\underline{\delta T}$, an electric field $\underline{E}$ will be developed with the thermopower being defined as $\delta T/E$. As shown in Figure 1c, the thermopower of a superconductor disappears at T_c. This property may be exploited in devices, say as switches, when superconducting materials with high T_c's become available.

There is also an abrupt change in thermal conductivity at T_c (Figure 1d). In some superconductors the thermal conductivity increases as the temperature decreases below T_c, while in other superconductors the thermal conductivity decreases with temperature below T_c. Determination of this property for specific superconductors yields significant information concerning the mechanism of the conduction process.

3 PERFECT DIAMAGNETISM OF SUPERCONDUCTORS, THE MEISSNER EFFECT

In 1933, Meissner and Ochsenfeld (7) reported that, upon cooling, a magnetic field is expelled from a normal metal specimen when it passes through T_c and becomes superconducting. This is the Meissner effect. The exclusion of magnetic lines of flux from an object in the superconducting state is shown schematically in Figure 3, where a penetration depth, designated as λ, is indicated. Typical values for λ are on the order of 50 nm.

The intensity, $\underline{B}$, of a magnetic field along a specific direction $\underline{i}$ within a body is given by

$$B_i = H_i + 4\pi M_i \qquad (\underline{6})$$

where $\underline{H}$ is the applied magnetic field and $\underline{M}$ is the magnetization. Upon dividing through by H_i, there results

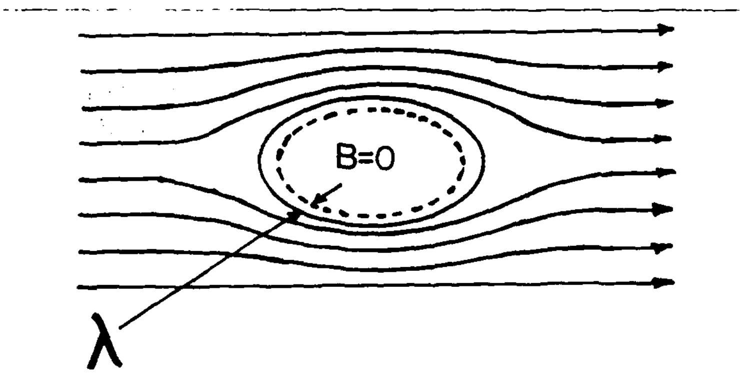

Figure 3. An object in the superconducting state in a magnetic field. The penetration depth, λ, is indicated by the dashed line.

$$B_i/H_i = 1 + 4\pi(M_i/H_i) \quad (\underline{6a})$$

where the ratio M_i/H_i is the susceptibility of the body towards induction in a field of strength H_i. The ratio is the volume magnetic susceptibility and it is denoted by χ. When placed in an inhomogeneous magnetic field, a diamagnetic substance will tend to move toward the weakest region (lowest density of magnetic lines of force) of the inhomogeneous field, while a paramagnetic substance will tend to move toward the strongest region of the magnetic field.

Since $\underline{B} = 0$ for superconductivity, then the lowest energy of the system is achieved when the superconducting body is in the weakest region of the magnetic field. The volume of the bulk superconducting sample is much larger than the volume of the penetration shell, $\underline{B} = 0$, and

$$\chi_i = -1/4\pi \quad (\underline{7})$$

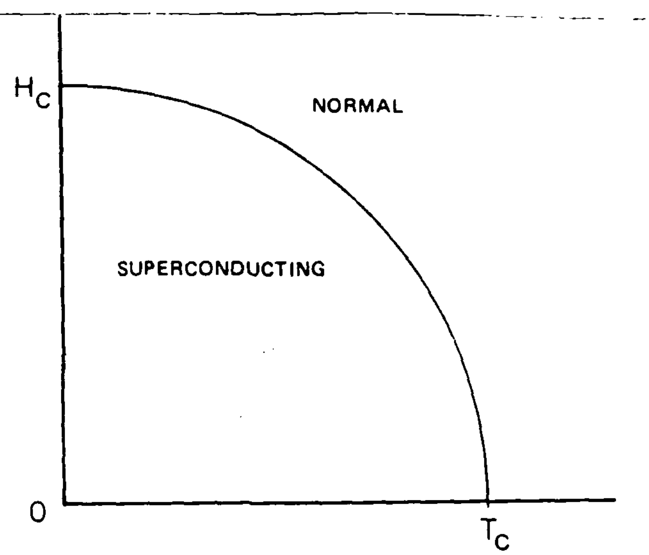

Figure 4. The phase diagram for a superconductor which shows the variation of the critical field H_c with temperature.

Thus, perfect superconductors exhibit perfect diamagnetism with a value of $-1/4\pi$.

The Meissner effect is reversible, and the temperature of the transition from the normal state to the superconducting state is dependent on the strength of the applied magnetic field. The critical field $\underline{H}_c$ is related to the thermodynamic energy difference between the normal and superconducting states. This energy difference is called the condensation energy of the superconducting state. The temperature dependence of the critical field is given by

$$H_c(T) = H_c(0)[1 - (T/T_c)^2] \tag{8}$$

and the phase diagram traced out by Equation (8) is shown in Figure 4, where it may be seen that the critical field $H_c = 0$ at $T = T_c$. The transition at zero field is second order, but the transition in the presence of an applied magnetic field is first order, since there are discontinuities in state properties as well as an associated latent heat.

In superconducting substances, a few elements and most alloys and compounds exhibit an incomplete Meissner effect and have broad magnetic transitions. These properties may be understood in terms of the theoretical developments which were evolving simulataneously with the experimental advances.

4 THEORETICAL DEVELOPMENTS

London Theory The discovery of the Meissner effect was soon followed by the work of F. London and H. London (8), who proposed

that the flux density $\underline{B}_x$ at a point $\underline{x}$ within a superconductor is given by

$$d^2B(x)/dx^2 = B(x)/\lambda_L^{\,2} \qquad (\underline{9})$$

where λ_L is the London penetration depth. The solution of the differential equation in one dimension gives

$$B(x) = B(0)\ \exp(-x/\lambda_L) \qquad (\underline{10})$$

which shows that the flux density decreases exponentially within the surface layer and essentially disappears when $\underline{x}$ is much greater than λ_L, a result which accounts for the Meissner effect. The London penetration depth is given by

$$\lambda_L = (mc^2/4\pi N_s e^2)^{1/2} \qquad (\underline{11})$$

If N_s is taken to be 9×10^{21} e/cm^3, a commonly accepted value for the number density of conduction electrons, λ_L is on the order of 10^{-6} cm. Values on this order of magnitude are obtained for many superconductors in weak magnetic fields.

Non-local Generalization of London Theory The London theory was unable to account for the properties of a number of superconductors, and it was necessary to modify the theory. Pippard (9) presented a successful model which is based on the uncertainty principle and the energy distribution of the electrons. The model recognizes that only those electrons with energy within kT_c of the Fermi energy will be involved in phenomena that occurs at T_c, and that those electrons have the Fermi velocity v_F. Thus, from the uncertainty principle, the range of momenta is $\delta p = kT_c/v_F$, and the range in position, or the characteristic length of the wavepacket ξ_o, is given by

$$\xi_o = ahv_F/2\pi kT_c \qquad (\underline{12})$$

where a is a constant of the order of unity and must be determined experimentally. Experiments on tin and aluminum (10) yield a value for a of 0.15. BCS theory yields a value of 0.18 for the parameter a.

Two Types of Superconductors It is possible to conclude immediately from the discussion in the previous sections that there are two types of superconductors, one type which may be described by the nonlocalized modification of the London model, and a second type by the original localized London model. These are called Type I and Type II superconductors, respectively, and they may be differentiated by their properties in an applied magnetic field. It is most revealing to consider the two types of superconductors in view of the additional theoretical developments presented in the following sections.

Ginzburg-Landau Theory and Abrikosov's Reversal In 1950 Ginzburg and Landau (11) presented a hybrid quantum mechanical-phenomenological treatment based on a complex wave function for the superconducting electrons utilizing the variational principle. The theory introduced a temperature-dependent coherence length $\xi(T)$, which is the same as the Pippard coherence length far from T_c, but which diverges at T_c. The theory was successful since it provided an explanation for the intermediate state of Type I superconductors which will be discussed below.

For typical pure superconductors, λ_L is approximately 50 nm, is about 300 nm, and the ratio $\chi_{GL} = \lambda/\xi$, which is a small

number, is the Ginzburg-Landau parameter. The surface energies implied by these dimensions are important in defining the domains of superconducting and normal phases and the intermediate state. The difference in surface energy between the superconducting and normal state is on the order of $\xi H_c^2/8\pi$, while the diamagnetic energy loss is $\lambda H_c^2/8\pi$. The positive surface energy results in a domain pattern for the intermediate state of a Type I superconductor with dimensions ranging from the microscopic coherence length ξ and the macroscopic sample size.

Arbikosov (12) considered the reverse situation in which $\lambda > \xi$, and χ is large. It is clear that the opposite situation from that described in the preceding paragraph must arise. That is, the subdivision into domains proceeds until it is limited by the microscopic length ξ. Superconductors which exhbit this property are called Type II superconductors. There are two critical fields for these superconductors. Consider the case of an initially superconducting body in an increasing applied magnetic field. At the critical field $H^c{}_1$ there is the onset of flux penetration, and this flux penetration increases with the applied magnetic field until a second critical field H_{c2} is reached. At values of the applied field above H_{c2} the body becomes normal. Since the energy required to exclude the magnetic field is reduced as a result of partial flux penetration, then Type II superconducing materials may have large values of H_{c2}. This property has permitted the utilization of superconducting materials in high-field solenoids and magnets.

Cooper Pairs Interactions between electrons in a metal in the normal state are usually ignored, and the resulting free electron model may be used to describe a wide range of properties of metals. Interactions between electons can not be ignored in superconducting state. In the superconducting state some of the electrons are bound together in pairs known as Cooper pairs (13). The Cooper pairs are governed by certain requirements of quantum mechanics, the most important of which may be the requirement that all of the Cooper pairs have the same value of total momentum. It may be shown that this property leads to the static electromagnetic properties of zero resistance, Meissner effect, and others. Other unpaired electrons can exist simultaneously with the Cooper pairs in the superconducting state, but the unpaired electrons are like electrons in the normal state. Currents carried by them are resistive, and their contributions to the magnetic susceptibility are very small. A Cooper pair is more stable than two unpaired electrons by the amount of the binding energy. This is energy of the superconducting gap introduced above.

Theory assumes that all of the electrons in a superconducting body are paired into Cooper pairs at 0 K in the absence of an applied magnetic field and an electric current. The Cooper pairs are broken up when energy is supplied to the metal, for examples, by application of an external magnetic field or by increasing the temperature. The population of unpaired electrons is proportional to $\exp(-E/kT)$. This provides an explanation for

many of the properties of superconducting substances, such as the exponential dependence of the specific heat, described above.

It is now possible to present a simple picture of a mechanism for superconductivity and the Cooper pairs. Consider one electron which is moving through the lattice of positive ions. The negative field of the electron polarizes and distorts the lattice of positive ions shown in Figure 5a to yield a region of excess positive ions (Figure 5b) which, in turn, attracts the second electron and yields an effective attractive interaction between the two electrons. If the attractive interaction is greater than the Coulomb repulsion, then superconductivity results. The role of electron-lattice interactions in the mechanism for superconductivity was first investigated by Fröhlich (14), and the suggestion was confirmed experimentally by the demonstration of an isotope effect on T_c and H_c (15).

An explanation may also be presented for the long lifetime of the persistent current. Since the flux is quantized, the current cannot decrease by an infinitesimal amount, but only by a quantized amount. Furthermore, superconductivity is a collective phenomenon, and the wave function involves all of the Cooper pairs. Thus, the quantized jump requires a simulataneous event of about 10^{20} pairs. Such an event is extremely improbable, and there is no decay of the persistent current.

<u>Bardeen, Cooper, Schrieffer (BCS) Theory</u> The theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer (5) in 1957, and which has been extended and refined by numerous

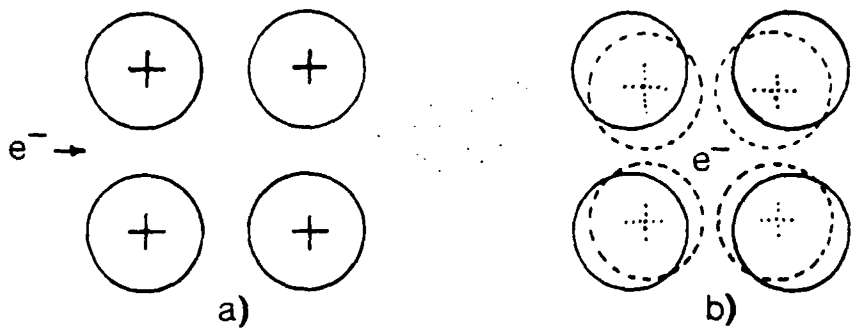

Figure 5. A simple model which shows the attraction of an electron to a lattice distortion.

subsequent studies, has been successful in explaining essentially all of the phenomena associated with the superconducting state. Such phenomena include specific heat, critical fields, tunnelling, and others. In addition, predictions by the theory have stimulated exploratory experimental work which has resulted in uncovering new phenomena associated with the superconducting state. A detailed examination of BCS theory will be given in the next paper (17). Here, only predictions concerning T_c will be considered.

In BCS theory, the transition to the superconducting state is given by

$$k_B T_c = (h/2\pi)\,\omega_o \exp[-1/N(0)V] \qquad (\underline{13})$$

where ω_o is the Debye frequency of the lattice, N(0) is the density of states at the Fermi surface, and V is the effective electron-electron attraction. McMillan (18) gives Equation (14) for strongly coupled superconductors

$$T_c = (\theta_D/1.45)\exp[-1.04(1 + \lambda)/(\lambda - \mu^*(1 + \langle\omega\rangle\lambda/\omega_o))] \qquad (\underline{14})$$

where θ_D is the Debye temperature, $\langle\omega\rangle$ is the average phonon energy, and μ^* is a Coulomb pseudo-potential. The parameter λ is related to the electronic density of states through the equation

$$\lambda = N(0)\langle I^2\rangle / M\langle\omega^2\rangle \qquad (\underline{15})$$

where $\langle I^2\rangle$ is an electron-phonon matrix element averaged over the Fermi surface, M is the atomic mass, $\langle\omega^2\rangle$ is the mean square phonon frequency.

Equation (13) yields clues concerning enhancement of superconduction transition temperatures. The Debye frequency may be obtained from a model in which the positive ions of mass M are attached to lattice points by springs having a force constant $\underline{k}$. From Hooke's law

$$\omega_o = (k/M)^{1/2} \qquad (\underline{16})$$

If the force constant is increased, then it may be seen from Equation (13) that T_c will increase, but there is a correlation between the force constant and V, the electron-electron attraction. An increase in $\underline{k}$ will lead to an increase in the rigidity of the lattice and, in turn, to a diminished distortion of the lattice by the electron. In the rigid limit $\underline{V}$ will become very small and T_c will vanish. A reduction in $\underline{k}$ will lead to a softer lattice, an increased electron-electron interaction, and initially an enhancement of T_c. There is a limit to enchancement of T_c by reducing $\underline{k}$. At some point the decrease in ω_o will outweigh the benefit gained from the increase in $\underline{V}$.

The Debye frequency can be increased by decreasing $\underline{M}$, the mass of the positive ions in the lattice. This feature of BCS

theory has stimulated interest in the design of systems (19) which utilize electron-hole pairs or excitons, because of their small $\underline{M}$'s. Calculations on proposed model systems have led to predictions of very high temperature superconducting transitions for systems described by Equation (13). It is unclear at this time whether the new high temperature ceramic superconductors exhibit BCS-type superconductivity.

Josephson Effect When a voltage difference is applied between two superconducting bodies separated by a insulating barrier of about 10^{-8} m, the unpaired electrons are able to tunnel across the barrier. The passage of electrons sets up a current which is characteristic of the magnitude and direction of the voltage difference. If the insulating barrier is made even thinner, then Cooper pairs may tunnel from one side of the barrier to the other side. However, there are important differences in the tunneling of unpaired electrons and the tunneling of Cooper pairs. The current from the Cooper pairs flows with zero resistance as in a single superconductor, and the electrons pass and current flows in the absence of a voltage difference. The system of two superconductors and a thin barrier behaves as a single supercon- ductor. As noted above, all Cooper pairs must have the same momentum and their density must be uniform. Thus, the Cooper pairs pass through the barrier in order to achieve a uniform density and equal momentum in the composite superconducting system. This behavior was predicted by Josephson (16) when he was a graduate student at Cambridge University.

The magnitude of the Josephson current is limited. If the current were above a sufficently large value, the Cooper pairs passing through the barrier may have enough energy to dissociate into unpaired electrons. The unpaired electrons do not move with zero resistance, nor do they move in the absence of a voltage difference. These physical constraints limit the magnitude of the Josephson current.

The Josephson effect is very sensitive to the presence of external magnetic fields. Changes of external fields on the order of one part in 10^{10} may be detected. Josephson junctions are widely used in ultrasensitive magnetometers and voltmeters.

5 THE IMTERMEDIATE STATE AND THE MIXED STATE

Effects of sample shape on the internal magnetic field of a body were ignored in Equation (6). They must now be taken into consideration. The magnetic field $\underline{H}^i$ within a body is related to the applied magnetic field $\underline{H}$ by the relationship

$$H^i = H - DM \tag{17}$$

where $\underline{D}$ is the demagnetization factor which depends on the shape of the specimen. For the purposes of this discussion, only spherical bodies, for which $\underline{D} = 4\pi/3$, will be considered. Along a specific direction in the magnetic field, $B = H^i + 4\pi M$ in the normal state. In the superconducting state, $\underline{B} = 0$, and for a Type I superconductor $H^i = -4\pi M$. Thus,

$$M = -H/(4\pi - D) \tag{18}$$

With $D = 4\pi/3$ for a spherical body, then

$$M = -3H/8\pi \qquad (\underline{19})$$

and

$$\chi = -3/8\pi \qquad (\underline{20})$$

Considering the spherical body, the maximum value of the internal field occurs on the equator, and it is given by

$$H^i = 3H/2 \qquad (\underline{21})$$

This has an important consequence for superconductivity in that the applied magnetic field will exceed the critical field when

$$H > 2H_c/3 \qquad (\underline{22})$$

and regions of the sphere must go normal. The entire sphere cannot go normal since $\underline{H} < \underline{H}_c$; the entire sphere can go normal only when $\underline{H} = \underline{H}_c$. Therefore, in the region $2H_c/3 < H < H_c$, both normal and superconducting regions of the material coexist. This state is called the <u>intermediate</u> state. The intermediate state consists of interleaved thin slabs of material in the normal and superconducting states, and it exists only in the presence of an applied magnetic field.

THE MIXED STATE The physical picture of the <u>mixed state</u> between H_{c1} and H_{c2} is that of a bundle of filaments of normal-state material in flux tubes arranged parallel to the applied flux lines, and these flux tubes are bathed in a sea of superconducting material. A schematic representation of the mixed state is given in Figure 6. Experimental manifestations of the mixed state include a discontinuity in the specific heat at the superconducting state-mixed state transition H_{c1}, and an abrupt

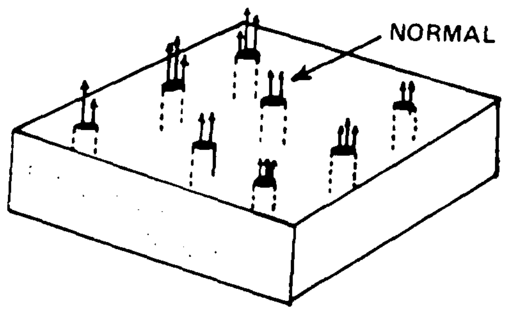

Figure 6. the mixed state of a Type II superconductor. The normal filaments inbeded in a superconducting mass are shown.

change in the specific heat at the mixed state-normal state transition H_{c2}.

The flux through a normal filament is accompanied by an electric current flowing around the filament in a plane perpendicular to the filament, something akin to a whirlpool. It is for this reason that the normal filaments are called vortex lines. The flux through a vortex line is quantized and has values equal to integral multiples of h/2e, the basic quantum of flux.

6 HIGH TEMPERATURE SUPERCONDUCTING CERAMIC MATERIALS

The Report That Stimulated the Current Interest On January 27, 1986, Muller and Bednorz (20) observed a strong decrease in resistivity upon cooling a barium-lanthanun-copper-oxide ceramic material. This ceramic, which was reported by Michel and Raveau

(21) in 1984, was selected for study because it exhibits a number of oxygen-deficient phases with mixed valence copper sites. It was anticipated that the itinerant electronic states between the non-Jahn Teller copper(III) and Jahn-Teller copper(II) ions would have considerable electron-phonon coupling and metallic conductivity.

Precedent Systems Superconductivity had been observed in other conducting oxides. The compound $Li_{1+x}Ti_{2-x}O_4$ was reported to have an onset temperature of 13.7 K in 1973 (22), and a T_c of 13 K was reported in 1975 for $BaPb_{0.7}Bi_{0.3}O_3$ (23). Both of these materials have mixed valence metals (Ti^{3+}/Ti^{2+} and Bi^{5+}/Bi^{3+}), and superconductivity occurs only over a small range of dopant concentration, x, with the highest transition temperatures occurring near metal-insulator phase boundaries.

The Confirming Evidence In the Conclusion of their paper, Bednorz and Muller state, somewhat tentatively, that "Samples annealed near 900 C under reducing conditions show features associated with an onset of granular superconductivity near 30 K". The onset of superconductivity was confirmed in single phase samples of $La_{2-x}Ba_xCuO_4$, and the results were announced in late 1986 by Chu and coworkers in Houston (22) and Tanaka, Kitazawa and coworkers in Japan (23). Based on powder X-ray diffraction data, the high temperature superconducting material with x = 0.15 was reported to be tetragonal and to have the layered K_2NiF_4 structure. The sample was prepared by a solid-state reaction of a mixture of lanthanum oxide, barium carbonate, and copper oxide

at temperatures above 900 C. The Japanese group found a superconducting onset at 32 K with zero resistance being attained at 22 K, with 30% of the sample showing bulk diamagnetism. The Houston group found the onset of superconductivity to be 39 K with full diamagnetism reached at 22 K with 10% of the sample fully superconducting. The Houston group also noted a sharp decrease in resistance near 70 K, but the phase responsible for the behavior was not determined. Both groups noted the critical temperature was dependent on the annealing conditions of the pressed pellets. Best results were obtained with pellets annealed under oxygen and then cooled in an oxygen atmosphere.

Communication of Results Following these announcements, there began a flurry of activity and many advances were made. Even rapid communication in scientific journals was slow compared to the pace of discoveries in high temperature superconductivity. However, newspapers and news magazines publish rapidly, and much of the new information was communicated through the pages of the Wall Street Journal, the New York Times, Science, Chemical and Engineering News, and others including the evening national news broadcasts. Sometimes the reports were premature, and some erronous information was reported.

Studies Under Pressure Samples with the K_2NiF_4 layered structure were subjected to pressure, and it was observed that the onset temperature was enhanced at a rate of 1 deg/kbar. This rate is about 100 times that of conventional superconductors (24). Chu and co-workers suggested that the large pressure effect might be

due to interfacial superconductivity (26) between a metal and a semiconductor where pressure can modify the coupling between the two components. They also discussed the role of the mixed valence copper ions in the superconducting mechanism.

It apparently occurred to several groups simultaneously to substitute strontium for barium, and there soon were several reports of near 40 K superconductivity (27,28). Strontium was considered promising because its ionic radius is closer to that of the lanthanum ion than is the radius of barium, and there could possibly be fine tuning of the copper(III):copper(II) ratio without distortion of crystal structure. The calcium analogue was also prepared and characterized (28), where an onset temperature of 23 K was found for single phase $La_{1.85}Ca_{0.15}O_4$. On the basis of the pressure studies by Chu and coworkers and arguments concerning internal pressure, it is not surprising that the calcium doped system has a suppressed T_c.

The next logical experimental tack was to replace the lanthanum ion by other dopants, and early successful syntheses utilizing yttrium yielded polyphasic material samples with transition temperatures in excess of 90 K (29). The superconducting phase was identified as a black material with formula $YBa_2Cu_3O_y$ (where y is now given as [7 - x]) (30). The timeline for research developments on high temperature superconductors is given later in these proceedings by Painter, et al.

Processing and Applications For superconducting materials to be useful in devices they must carry substantial electrical currents

and they must withstand relatively large applied magnetic fields. In May, 1987 workers at IBM's Thomas J. Watson Research Laboratory prepared a thin-film crystalline specimen of the high T_C material and found that it could conduct 100,000 amperes per square centimeter at 77 K. The goal is 1,000,000 amperes per square centimeter. This result points to applications of the these new materials, for example in SQUIDS, as demonstrated by IBM and the National Bureau of Standards.

Much effort has been expendend in attempts to make wires out of the ceramic materials. The approach at AT&T Bell Laboratories was to place the powdered oxide in a thin metal tube, which was then stretched, shaped, and fired to yield a superconducting "wire", while at Argonne the powder was mixed with a binder, shaped, and fired. The binder burned away during the firing process, and the superconducting wire was left as shaped.

There are numerous applications for high temperature superconducting materials. Superfast computers could be produced using Josephenson junctions which are more than 10 times as fast as conventional switches. Small, but more powerful magnets could be produced from superconducting wires, and these could be used in numerous transportable devices currently not possible with heavier conventional systems. Frictonless devices, including levitated trains, may also be envisaged. A detailed consideration of applications of high temperature superconductors is presented by Blaugher in a later paper in these proceedings.

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